High voltage $Na_3V_2O_{2x}(PO_4)_2F_{3-2x}$ (0<x<1) cathode materials for Na-ion batteries

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Sodium-ion batteries have arisen as good candidates to become alternative systems that could complement commercial Li-ion systems [1]. The use of Na instead of Li in rocking chair batteries could mitigate the possible shortage of lithium in an economical way. For this purpose, the search for commercially viable Na-ion batteries demands finding and optimizing new electrode materials and electrolytes.

Among the possible cathodic materials, the family of compounds $Na_3V_2O_{2x}(PO_4)_2F_{3-x}$ presents high operating voltages and specific capacity values, which are key parameters to get a high energy density battery [2].

Two different series of sodium-vanadium fluorophosphate samples were prepared. In the first one, the carbon content used in the synthesis varied, leading to mixed valence V^{3+}/V^{4+} compounds where 0<x<1 for the $Na_3V_2O_{2x}(PO_4)_2F_{3-x}$ family. The second set of samples was prepared by a different synthesis method with no added carbon in order to get the V^{+4} $Na_3V_2O_2(PO_4)_2F$ phase (x = 0).

Structural characterization of the composites was performed by powder X-ray diffraction (XRD). Magnetic susceptibility measurements and EPR (Electron Paramagnetic Resonance) polycrystalline spectra were necessary for the determination of the oxidation state of the vanadium. The morphology of the materials was analyzed by Scanning Electron Microscopy (SEM) and the electrochemical measurements were conducted using Swagelok-type cells versus a metallic sodium anode. Ex situ XRD data for charged and discharged electrodes at selected voltages allowed us to study more deeply the structural evolution of the material during cycling.

The electrochemical results of mixed-valence V^{3+}/V^{4+} compounds showed high operating voltages (3.6 and 4.1 V vs. Na/Na^+), high capacities, good cyclability and excellent rate capabilities (figure 1). Mixed-valence vanadium and the presence of carbon enhanced electrochemical performance of the materials.

A comparison between the up-to-date bibliography [3,4] and the electrochemical data obtained from both the mixed valence and V^{4+} materials will be established. The need of using characterization techniques linked to magnetic properties in order to know the materials used as electrodes for sodium-ion batteries will be discussed.

To sum up, it is worth noting that these materials present several advantages, such as having an easily scalable synthesis process that favors, if desired, an in-situ carbon coating of the samples. This feature, together with their excellent electrochemical performance makes this family of materials very attractive for its use as cathode for Na-ion batteries.

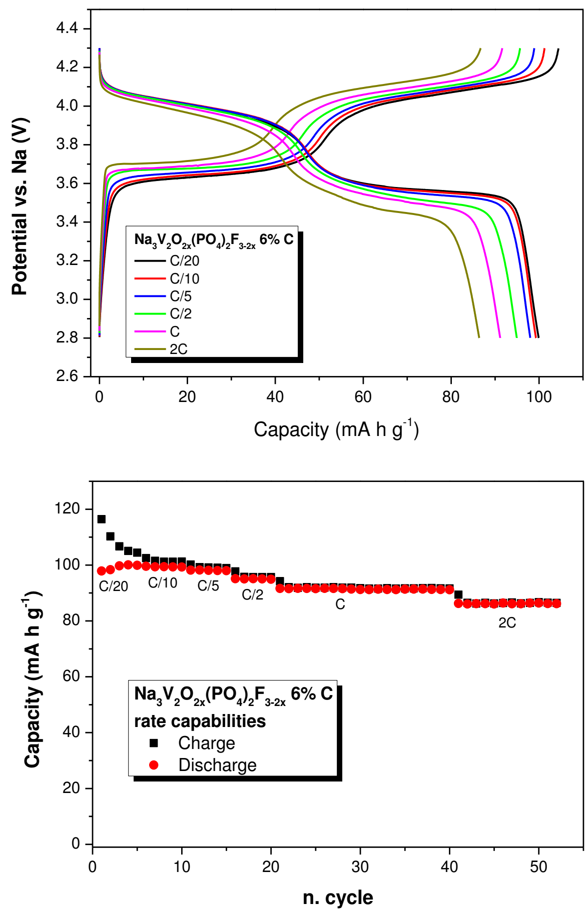

Figure 1. (top) Charge-Discharge curves, and (bottom) cycle performance of mixed valence V^{3+}/V^{4+} sample at different C rates.

References

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